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(54) Title: METHOD OF INHIBITING RESERVOIR SOURING BY BACTERIA

(57) Abstract

A method of inhibiting the growth of bacteria, especially anaerobic sulphate reducing bacteria, within oil and gas reservoirs by the addition of peroxy compounds to injected flood water is described. Suitable peroxy compounds include one or more of methyl ethyl ketone peroxide, cyclohexanone peroxide, acetyl acetone peroxide, diacetone alcohol peroxide, dibenzoyl peroxide, ditertiary butyl peroxide, tertiary butyl peroxide, hydrogen peroxide, tertiary butyl peroxy benzoate, inorganic and organic peroxycarbonates, or functional equivalents or derivatives of these compounds. The peroxy compound additives have the advantage of being thermally sensitive such that penetration into the reservoir and placement in strategic zones can be achieved leading to sterilisation deep within the reservoir. The compounds may also be tailored to optionally scavenge hydrogen sulphide produced by bacterial growth from the reservoir fluids.

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# METHOD OF INHIBITING RESERVOIR SOURING BY BACTERIA

The present invention relates to a method of reducing the souring of hydrocarbons due to bacterial production of hydrogen sulphide gas.

During the production of hydrocarbon fluids, such as oil or gas, it is common practice to flood the reservoir holding the hydrocarbons with water to enhance production by maintaining pressure as oil and/or gas is removed and to "sweep" hydrocarbons which would normally remain within the reservoir to the collection well.

The source water used in such flooding operations is frequently a natural brine and in the case of offshore oil and gas production is normally sea water.

Flooding of a reservoir with natural brines usually has undesirable consequences since the brine may be responsible for the introduction and/or accelerated growth of bacteria within a reservoir as follows:

1. Bacteria within the brine flood water are introduced to the reservoir and find a hydrocarbon

source (for example, oil). The oil may then be metabolised by the bacteria allowing the rapid growth of bacterial populations.

2. Bacteria which may be naturally present in the reservoir in dormant form will receive a nutrient supply due to the introduction of the flood water. Again, the increased nutrient supply will promote bacterial growth within the reservoir.

Generally, anaerobic conditions will exist in the reservoir, and bacteria able to cope with low amounts of oxygen or the absence of oxygen will preferentially proliferate. Generally, the most dominant form of bacteria is the so called sulphate reducing bacteria (SRBs). SRBs metabolise sulphates from the injected flood water and produce hydrogen sulphide gas as a waste product.

The hydrogen sulphide generated will become partitioned in both the oil/gas and water phases within the reservoir. More importantly, however, the hydrogen sulphide would normally be co-produced in the fluids at the producing well.

The process of hydrogen sulphide production by bacteria is known as reservoir souring. The consequence of this process is a gradual increase in hydrogen sulphide content within the produced fluids.

Hydrogen sulphide is highly undesirable in the produced fluids since it is corrosive and toxic. Consequently, the presence of hydrogen sulphide as a contaminant adversely affects the sales quality of the exported oil and gas.

It is thus normal practice within the industry to attempt to prevent bacterial growth within the reservoir by the addition of biocides to the injected water in order to sterilise the system and therefore prevent proliferation of bacteria.

Typical biocides include chlorine, aldehydes such as gluteraldehde, thiazolines and quaternary amines.

However, the continual addition of biocide is frequently too costly to practice and more usually a sweep dosage at suitable intervals is used to sterilise the system.

Despite biocide addition, it is almost impossible to prevent the introduction of all bacteria to a reservoir and a reduced rate of souring may still occur.

Additionally, due to the surface active nature of the majority of biocides, the biocides are readily absorbed to the surfaces of minerals such as clays found in reservoir sands. It is therefore not normally possible to achieve penetration of the biocide deep into a reservoir.

Hence elimination of bacteria naturally present within a reservoir or introduced by the flood water and moving with oil/water flood front boundary is normally not achievable using conventional biocides.

One way to obtain an end product having acceptably low levels of hydrogen sulphide is the removal of that gas by treating the extracted hydrocarbons. This will normally require the installation of process equipment to remove the hydrogen sulphide gas by, for example, flaring, treating with amine scrubbers to absorb the

gas or addition of chemicals to scavenge by reaction to produce a neutralised compound.

However, all such methods of hydrogen sulphide removal considerably increase the cost of production and are generally considered to be undesirable.

In summary, it can be seen that a number of options exist to prevent build up of hydrogen sulphide in the produced fluids:

a. inhibit the growth of bacteria within the reservoir by chemical addition to the flood water;

b. scavenge the evolved hydrogen sulphide within the reservoir to prevent production with recovered fluids.

However, as indicated above, it is apparent that such treatments are not practical using conventional biocides or scavengers from performance and/or cost constraints.

We have now found that the use of peroxy compounds (which are not normally thought of as biocides) are ideally suited to the treatment of bacterially contaminated reservoirs. The peroxy compounds can both destroy resident bacteria and also act to remove hydrogen sulphide already generated.

In one aspect, the present invention provides a method of inhibiting the growth of bacteria in a hydrocarbon reservoir, said method comprising introducing a peroxy compound to said reservoir.

In another aspect, the present invention provides a

method of combatting the generation of hydrogen sulphide in a hydrocarbon reservoir by sulphur reducing bacteria, said method comprising introducing a peroxy compound to said reservoir.

The complementary actions of the peroxy compounds arise from the oxidising potential of such compounds and the generation of free radicals as the peroxy compound decomposes.

The peroxy compounds for use in the present invention are normally stable neutral compounds which therefore show minimal absorption to the reservoir minerals and can therefore penetrate deep into the reservoir carried by the flood water.

The peroxy compounds of interest may be selected to decompose at the particular temperatures encountered within the reservoir (usually elevated temperatures relative to the ambient). Particular activation temperatures can be engineered by selection and/or modifications of the peroxy compounds used, to allow the selective placement of compounds within reservoirs of widely differing temperatures.

Decomposition of the peroxy compounds leads to the generation of free radicals which are highly aggressive towards living cells. The free radicals cause damage and ultimately destroy cells such as bacteria.

In addition, the generation of coincident oxidising species occurs and these oxidising species will react with hydrogen sulphide leading ultimately to formation of harmless sulphates in the produced fluids.

The peroxy compounds therefore have the advantages of

being selective to the destruction of bacteria without being lost to the reservoir by absorption or decomposition prior to deep penetration. The peroxy compounds also remove encountered hydrogen sulphide to prevent continued production within the recovered fluids.

The type of peroxy compounds useful for this invention contain the chemical grouping -O-O- and may be generally described by the formula:

$$R{-}O{-}O{-}R'$$

where R and R′ may be hydrogen, alkyl or aromatic groups (including substituted cyclic and branched groups), oxygenated hydrocarbon chains such as carbonate or ketone, or other groups which will result in stabilisation of the peroxide linkage.

Modifications to the structure of R and R′ alter the solubility characteristics and thermal stabilities of the peroxides which allows for selective placement and activation in reservoirs of differing temperatures and can also allow penetration of oil layers by selection of oleophilic peroxides should this be desirable.

The reaction occurring by thermal decomposition of the peroxy compounds leads to the generation of free radicals, thus:

$$R'{-}O{-}O{-}R \xrightarrow{\Delta H} R'{-}O\bullet + R{-}O\bullet$$

The generated free radicals may undergo various reactions leading to complex organic products but all such reactions lead to cellular attack and therefore have biocidal properties.

In addition, the reaction:

$$R\text{-}O\bullet + H_2S \rightarrow R\text{-}OH + HS\bullet$$

can take place to give a reactive thiol free radical (HS•) which will bind to organic materials such as crude oil or bacterial cells to eliminate free $H_2S$ from the system.

A further decomposition reaction can lead to the formation of free oxygen which again limits bacterial activity by altering the oxygen free conditions necessary for SRB growth.

The described peroxy compounds therefore provide advantageous multifunctional behaviour which can prevent reservoir souring.

Viewed from a further aspect, the present invention provides the use of a peroxy compound to inhibit bacterial growth within a hydrocarbon reservoir or to reduce the hydrogen sulphide content of a hydrocarbon fluid.

In addition, the present invention also provides a hydrocarbon fluid (eg oil or gas) containing a peroxy compound or a reactant thereof as an additive.

The range of useful peroxy compounds to be applied to a reservoir may be characterised by a self accelerating decomposition temperature (SADT) where a critical value will cause the compound to decompose at an accelerating rate yielding the free radicals necessary for biocidal activity.

However, the value may be adjusted by the inclusion of

accelerators or inhibitors which allow a peroxy compound to be utilised at temperatures above or below this figure.

Examples of suitable peroxy compounds which may be added to a reservoir flood water for the purpose of the invention include, but are not limited to:

Methyl ethyl ketone peroxide,
Cyclohexanone peroxide,
Acetyl acetone peroxide,
Diacetone alcohol peroxide,
Dibenzoyl peroxide,
Ditertiary butyl peroxide,
Tertiary butyl peroxide,
Hydrogen peroxide,
Tertiary butyl peroxy benzoate,
Inorganic and organic peroxycarbonates, or

functional equivalents or derivatives of these compounds. A mixture of such compounds may be used.

Other compounds which are known to generate oxidative free radicals by thermal or catalytic decomposition will show similar biocidal activity.

Generally, the peroxy compounds will be added to the flood water prior to injection into the reservoir.

CLAIMS

1. A method of inhibiting the growth of bacteria in a hydrocarbon reservoir, said method comprising introducing a peroxy compound to said reservoir.

2. A method of combatting the generation of hydrogen sulphide in a hydrocarbon reservoir by sulphur reducing bacteria, said method comprising introducing a peroxy compound to said reservoir.

3. A method as claimed in either one of Claims 1 and 2, wherein the peroxy compound may consist of a water soluble or water dispersable inorganic or organic based peroxy compound.

4. A method as claimed in any one of Claims 1 to 3, wherein the peroxy compound may be a peroxide, hydroperoxide, peroxycarbonate, peroxysulphate or other peroxide based complex.

5. A method as claimed in any one of Claims 1 to 4, wherein the peroxy compound may be selected from one or more of methyl ethyl ketone peroxide, cyclohexanone peroxide, acetyl acetone peroxide, diacetone alcohol peroxide, dibenzoyl peroxide, ditertiary butyl peroxide, tertiary butyl peroxide, hydrogen peroxide, tertiary butyl peroxy benzoate, inorganic and organic peroxycarbonates, or functional equivalents or derivatives of these compounds.

6. A method as claimed in any one of Claims 1 to 5, wherein said peroxy compound is added to the reservoir flood water.

7. A method as claimed in any one of Claims 1 to 6, wherein the peroxy compound is selected to decompose at a temperature of the reservoir.

8. A method as claimed in any one of Claims 1 to 7, wherein a co-additive may be optionally added to the peroxy compound to either inhibit or accelerate decomposition of the peroxy compound as a function of temperature.

9. Use of a peroxy compound to inhibit bacterial growth within a hydrocarbon reservoir.

10. Use of a peroxy compound to reduce the hydrogen sulphide content of a hydrocarbon fluid.

11. Hydrocarbon fluid containing a peroxy compound or a reactant thereof as an additive.

# INTERNATIONAL SEARCH REPORT

International application No. PCT/GB 97/01537

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC6: C10G 27/12, A01N 37/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C10G, A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, APIPAT

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | AU 53138/79 A1 (BIOLEX CORP.), 28 May 1981 (28.05.81), page 6, line 35 - page 8, line 1 - line 16, claims 1-7 | 1-11 |
| | -- | |
| A | EP 0082513 A1 (PEROXID-CHEMIE GMBH), 29 June 1983 (29.06.83) | 1-11 |
| | -- | |
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☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

06/08/97

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| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| AU 53138/79 A1 | 28/05/81 | NONE | |
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